

CATALYST TAILORING FOR COAL DERIVED LIQUIDS

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The United States energy requirements have refocused attention on coal processing for fuels in forms other than for direct combustion. Hydrogenation of coal and coal liquids is included in this renewed interest. Many reports (1, 2, 3) are available on studies directed toward upgrading coal and coal liquids by hydrogenation. A good portion of these efforts is directed toward testing and developing various active metals for catalysts. The nature and character of the carrier or support material have received somewhat less attention. With coal liquids, removal of nitrogen is particularly important, yet almost no work has been reported in this area.

The work reported in this paper is part of an overall program to specifically tailor catalysts for upgrading coal derived liquids. Attention here is given to the removal of sulfur and nitrogen atoms from a coal liquid.

The Pittsburgh & Midway Coal Mining Company has developed a process to produce an ashless, low sulfur fuel from coal (4, 5, 6). Light oils and gas oils are also co-products from this solvent refined coal process. However, the nitrogen and sulfur in these oils must be removed if these oils are to be of value for further fuel processing. Our catalyst development work was at first directed toward upgrading these oils by the removal of their heteroatoms, particularly sulfur and nitrogen.

Since only limited quantities of the oil products from the solvent refined coal process were available from actual laboratory and pilot production, our initial work was performed on a coal liquid which has somewhat similar properties. For a comparative basis, results are reported on two catalysts which were obtained from Nalco Chemical Company. The first objective is to compare operating characteristics of these two catalysts, which have essentially identical composition but contain a rather different pore volume and pore size distribution. The catalyst properties are discussed below. The apparatus used in the study was a downflow, packed-bed reactor; details are also given below under experimental.

Feedstock. The feedstock used in this experiment was a raw anthracene oil which was obtained from the Reilly Tar & Chemical Corporation. The feed properties are given in Table 1, showing that the sulfur level was 0.45 wt% and nitrogen was 0.8 wt%.

Catalysts. The two Nalco Catalysts which were tested were Nalco 474 and Sphercat 474. These were both compounded with 3.5 wt% of cobalt oxide and 12.5 wt% molybdenum oxide on alumina support. Pore volume was 0.463 cc per gram for the Nalco 474 and 0.981 cc per gram for the Sphercat 474. As shown in Figure 1, the Sphercat has a bimodal pore distribution with modes at about 30 angstroms for micropores and at 850 angstroms for macropores. The Nalco catalyst had a singular and rather narrow distribution at about 33 angstroms. These pore size distributions were determined from mercury penetration data to 60,000 psi. Figure 1 is a plot of $dV/d(\ln r)$, where

V = accumulative pore volume
 r = pore radius

The total surface area per gram was about the same for both catalysts, and an 8/10 mesh size was used. Properties are shown in Table 2.

Apparatus. The experimental apparatus is diagramed in Figure 2. Anthracene oil was fed from a Ruska pump through preheated lines into the reactor. The feed oil was contacted with hydrogen just before the reactor inlet. The $\frac{1}{2}$ inch diameter reactor was packed with from 13.7 to 15.8 grams of catalyst and had pre- and postheat zones of inert material. The reaction temperature was monitored with a traversing thermocouple in a thermowell located within the center of the reaction tube. Excellent temperature control was obtained by three massive aluminum blocks which were grooved and wound with resistance heating wires. The larger center block was maintained at the desired temperature by a controller, while the smaller top and bottom blocks were controlled manually to obtain flat temperature profiles. A typical profile is shown in Figure 3. Hydrogen flow was monitored by observing rates on a wet test meter placed in the exit line. The desired operating pressure was controlled by a back pressure regulator and was read on a Heise gage located at the reactor inlet.

Analysis. Sulfur analyses were made on a Leco Model 634-700 automatic sulfur analyzer which had been modified for relative low sulfur determinations. These modifications include slight adjustment in the techniques which are outlined in ASTM D 1552-64, and the addition of sodium azide to eliminate nitrogen interference. Nitrogen analyses were made by a commercial laboratory and by our own laboratory, both using a modified micro Kjeldahl technique. Distillations were performed according to ASTM D 1160 technique. Catalysts properties were obtained from information supplied by Nalco Chemical Company and by commercial laboratory analyses.

Experimental. Experiments were made over a temperature range of 600 to 800°F, a total pressure range of 500 to 2000 psig, and space times (based on reciprocal liquid hourly space velocities) of $\frac{1}{4}$ to 2 hours. Most of the experiments were made on Nalco 474 over these variable ranges, and the comparison of the two catalysts was made from data taken at a fixed set of conditions. These conditions were 700°F, 2000 psi pressure, and about one-hour space time. These two comparative runs each covered a total of over 40 hours oil-catalyst contact. There were several planned shutdowns during these experimental runs. The catalysts were presulfided before use. For ease of comparison, the experiments on these two 40-hour runs were performed at identical weight hourly space velocities. This means that the volume hourly space velocities were different because of a difference in the catalyst pellet density.

In trickle flow reactors there is always a question of adequate contacting

of oil and solid particles. In addition to other variables, particle size, superficial oil velocity, and superficial gas velocity may influence the nature of oil-solid contacting. Tests were made by varying superficial gas velocity by a factor of 10, and no noticeable influence on desulfurization or denitrogenation was observed over this range. There seemed to be adequate contacting of oil and solids for the particle sizes and velocities used within the study.

Results. The pressure, time and temperature effects for desulfurization of the Nalco 474 catalyst are shown in Figures 4, 5, and 6. The rate of desulfurization is rapid within the first 0.5 to 1.0 hours space time, and becomes quite slow thereafter. The maximum desulfurization appears to be fixed at around 90-95 percent removal. However, at 90 percent removal of sulfur from the feed oil, the product sulfur level is in the range of 400 parts per million. This is within the region where reproducibility of sulfur analyses is becoming limited by the techniques used. The effect of pressure between 500 and 2000 psi on desulfurization is the greatest at 600°F operation; whereas, there was little pressure response noted at 700 and 800°F. The multiple points shown in Figure 6 for 700°F and one hour space time were duplicates except for a difference of over 60 additional hours of oil-catalyst contact. There was negligible loss of catalyst desulfurization activity during the 70 plus hours total oil-catalyst contact of this sequence of experiments.

The extent of hydrocracking with the Nalco catalyst is shown in Table 3 for operation at 800°F and two hours space time. These represent maximum temperature and times used in the experiments. The extent of hydrocracking is quite dependent upon the pressure of the experiment. Two reference points are listed in the table. One shows the amount of 650°F+ material in the feed which was converted to lower boilers, and the other reference point is the amount of 500°F+ material converted. Note that the data indicate significant quantities of material boiling above 650°F were converted to lower boilers, but very little of this was converted to material boiling below 500°F. However, at 2000 psi and 800°F, significant hydrocracking to -500°F material occurs. The extent of hydrocracking at lower temperatures and pressures was, of course, lower than those shown in Table 3. Very little hydrocracking takes place at 600°F.

Shown in Figure 7 is a comparison of the desulfurization levels for both the Nalco 474 and the Sphercat 474 catalysts. The desulfurization activity of the Nalco catalyst achieved a level of about 92 percent removal after 10 hours on oil, and remained relatively steady between 88 to 90 percent for over 50 hours. The Sphercat 474 showed almost identical desulfurization characteristics from ten through 42 hours on oil. The Sphercat data tends to be slightly higher than those of the Nalco; however, within the limits of this study this is not shown unequivocally. For both catalysts, there is no noticeable loss in desulfurization over 40-50 hours.

Figure 8 presents a comparison of the two catalysts for denitrogenation for over 40-50 hours oil-catalyst contact. Although the Nalco 474 catalyst maintained a stable denitrogenation activity, the Sphercat denitrogenation activity dropped rather quickly. Further, the ability of the Sphercat to remove nitrogen was always lower than that of the Nalco catalyst. In both cases the ability to remove nitrogen was limited. For Nalco this was no more than 60 percent at best; and for the Sphercat, no more than about 50 percent.

Discussion. The hydroprocessing of heavy liquid feedstocks for sulfur and nitrogen removal is representative of one of the most complex reaction

systems to be encountered. With solid, liquid and vapor phases present, there are many resistance zones which can limit mass transfer. Several critical dimensions of the reaction system must be considered. Among these are:

- reactor bed length and diameter
- catalyst particle size
- liquid film thickness surrounding the solids
- catalyst pore size and pore size distribution
- size of the sulfur and nitrogen compounds

In processing heavy feedstocks the catalyst pores will be filled with liquids. The sulfur and nitrogen compounds must then transfer from the liquid film surrounding the pellets into the relatively quiescent liquid within the pores. These molecules then must diffuse through the liquid to the active solid surface. Hydrogen must transfer from the bulk gas phase into the external liquid film, and finally through the liquid filled pores to the reaction surface. There are three primary zones which may control the overall removal of heteroatoms:

1. Interparticle Resistance - the exterior catalyst surface must be supplied with reactants; gaseous or liquid.
2. Intraparticle Resistance - the reactants must diffuse through the porous catalyst structure.
3. Surface Phenomena - molecules must adsorb, desorb and react on the surface.

In this coal liquid study with the catalyst pores filled with liquid, and assuming that many of the sulfur and nitrogen containing molecules are relatively bulky species, the most likely controlling resistance of the overall process is the transport of these bulky molecules through the pores.

Interphase and interparticle mass transfer in the form of adequate liquid distribution over the solids, hydrogen transfer from the bulk phase, and liquid supply to the external pellet surface were probably not controlling. This is shown, in part, when no effect was observed when hydrogen flow rate was varied by a factor of ten. Liquid distribution over solids is partly controlled by the ratio of reactor diameter to that of the catalyst (7). Numbers from 5 to 25 have been suggested for this ratio for adequate liquid distribution. The value in this study was 6.2. The effect of backmixing in trickle-flow laboratory reactors has recently been discussed by Mears (8). For freedom from backmixing a value of 350 has been suggested as a conservative estimate for the ratio of reactor length to particle size. The value in this study was about 144.

Although specific experiments were not performed on various particle sizes in order to determine a catalyst effectiveness factor, a first estimate suggests that the effectiveness factors for both desulfurization and denitrogenation of this coal liquid fall between 0.3 and 0.6. These numbers are based on only very approximate estimates of effective diffusivities. Typical desulfurization data taken under similar conditions, but on petroleum stocks fall into this range. There are, of course, significant differences between these general feed types.

For catalysts operating with effectiveness factors in this range, significant reactant concentration gradients can exist within the solids. The smaller and more mobile hydrogen molecules can penetrate far deeper into the catalyst pellets than can the much larger liquid reactants. Some of the larger nitrogen and sulfur containing molecules believed to be in high temperature

coal tar liquids are shown in Table 4 (9). There is, of course, a spectrum of molecular sizes, and these shown in Table 4 may only be representative of the larger sulfur and nitrogen species, but not necessarily in anthracene oil. For illustrative purposes, consider a reactant molecule with a characteristic or critical diameter in the range of 10-15 Å. For comparison, critical diameters for smaller compounds are shown in Table 5. When the size of the diffusing molecules begin to approach the pore size, then diffusion becomes strongly retarded. This sort of retardation was probably operative with both the Nalcomo and Sphericat 474 catalysts. As shown in Figure 1, the micropores of both catalysts have modes at about 30 Å radius. Thus it seems likely that a significant diffusion limitation exists for the larger reactant species.

The end result to be expected is relatively low active surface utilization which is revealed in a low effectiveness factor. Values of 0.3 or lower can be expected. In a trickle-flow reactor operating on a gas oil, effectiveness factors as low as 0.3 were reported (10). The major limitation was said to be sulfur compound transport within the pores. Molecular sizing effect was shown by Maxted and Elkins (11) in comparing catalytic hydrogenation of cyclohexene and ethyl crotonate with supported platinum. Supports of varying pore structure were equally active in hydrogenating the smaller cyclohexene molecule; however, those of fine pore structures revealed a lower activity for hydrogenating the larger ethyl crotonate molecule.

In comparing the performance of the Sphericat and Nalcomo catalysts, the increased pore volume and bidispersed character of the Sphericat provided no advantage in the limited tests performed. Considerable evidence suggests that first expectations would be that the macropore structure and increased pore volume of the Sphericat would provide greater access to the active surface; thus, increased desulfurization and denitrogenation. At least gaseous diffusion is enhanced by increased macropore volumes (12, 13). In desulfurization studies on straight-run Kuwait gas oil, an increase in catalyst macropores resulted in increased sulfur removal (14). Significantly, these experiments were conducted under liquid filled pore conditions. In work by Beuther et al. (15), the hydrodesulfurization of a light catalytic gas oil increased with an increase in catalyst porosity up to a maximum and then fell off. However, this comparison was made at a constant liquid hourly space velocity such that a simple loss in total catalyst mass would eventually offset any gain in porosity enhancement. In a recent study on desulfurization of diesel oil, those catalysts with larger pore volumes were reported to be more active in removal (16).

Contrary to this evidence, the advantages of increased pore volume were not shown on the Sphericat catalyst when processing this coal liquid. Anisotropic structure of the spherical catalyst is a possible explanation. Satterfield et al. (7) reported that spherical, palladium-on-alumina pellets showed a layering effect with respect to pore regions. These pellets contained an outer, fine pore region followed by a coarser section, and then a second fine pore region. If the Sphericat catalyst used in this study contained such a micropore outer region, then at low effectiveness factors there would be no advantage shown by those coarser regions which contribute to the higher pore volume. Satterfield has also mentioned this anisotropic pore layering effect in another study utilizing spherical catalysts (17). Such characteristics could possibly be unique to spherical catalyst support preparation techniques.

Figure 1 indicates that both catalysts have a micropore structure, in the order of 30-35 Å radius, which will account for most of the 270 m² of surface per gram of catalyst. Note in Figure 10 that the cumulative pore

volume curves are quite similar through about 0.37 cc/g (at about 45 \AA^2). Up through this point, most of the surface will have been accounted for. The cumulative volumes beyond contribute relatively little to total surface area (volume in a hypothetical pore cylinder will be increasing with radius squared, but area with radius to only the first power). Apparently the desulfurization limitations lie in the micropore region and not in the macropore region.

The cause of the difference in denitrogenation behavior of the two catalysts is difficult to resolve. Thus far, the effective reaction zones within these catalysts have been assumed to be the same. The initially lower nitrogen removal of the Sphericat suggests that the pretreatment might have been sufficiently different to affect nitrogen but not sulfur removal. In any case, there is a loss in activity which indicates a greater carbon formation by the Sphericat. The immediate cause of this increased cracking to form carbon is not evident. A relative measure of the amount of carbon formed on each catalyst was not available since experiments were still underway on the Sphericat.

In general, satisfactory nitrogen removal is more difficult to obtain than that for sulfur. From studies made on pure compounds, the removal of nitrogen from large heterocyclic rings is a step-wise hydrogenation process (18, 19). Carbazole is a nitrogen containing compound found in coal liquids. Flinn, et al. (18) discussed a five-step, dual path sequence leading to the denitrogenation of this compound. This is shown in Figure 9 along with a sequence for pyridine. These complex sequences for denitrogenation are apparently more sensitive to subtle catalyst property differences that, in turn, have little effect in desulfurization.

Relatively little work has been done to tailor catalysts and support properties explicitly to removal of heteroatoms from coal liquids. Although a vast amount of work has been given to processing petroleum stocks, and some of this information can be applied to coal liquids, there are significant differences between coal and petroleum derived materials which require specific catalyst tailoring for these coal liquids. The removal of nitrogen from coal liquids will demand particular attention.

TABLE I
FEED OIL PROPERTIES

Carbon wt%	_____	90.65
Hydrogen	_____	5.76
Sulfur	_____	0.45
Nitrogen	_____	0.8
Ash	_____	Nil
API Gravity @ 60°F	_____	-7

*Distillation

Initial	_____	380°F
10 Vol%	_____	450
30	_____	570
50	_____	650
70	_____	700
90	_____	815

*Normal boiling data determined from ASTM D 1160 data.

TABLE 2
CATALYST PROPERTIES

	<u>Nalcomo 474</u>	<u>Sphericat 474</u>
*CoO, wt%	3.5	3.5
*MoO ₃ , wt%	12.5	12.5
Support	Alumina	Alumina
Pore Volume, cc/g	0.463	0.981
*Surface Area, m ² /g	270	270
Pellet Density, g/cc	1.31	0.77
*Packed Bed Density, g/cc	0.73	0.48
Pellet Size	8/10 Mesh	8/10 Mesh

*Nalco Data

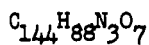
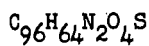
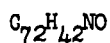
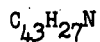
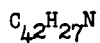
TABLE 3
 Hydrocracking On
 NALCOMO 474 at 800°F,
 2 Hr. (liquid hourly space time)

<u>Pressure, psi</u>	<u>500</u>	<u>1000</u>	<u>2000</u>
*Percent Loss in 650°F+ Boilers	20	36	57
Percent Loss in 500°F+ Boilers	5	8	20

$$\text{*Percent Loss} = \frac{(\text{fraction } 650^{\circ}\text{F+ boilers in feed}) - (\text{fraction } 650^{\circ}\text{F+ boilers in product})}{(\text{fraction } 650^{\circ}\text{F+ boiler in feed})}$$

TABLE 4

Large Coal Liquid Compounds Containing Heteroatoms



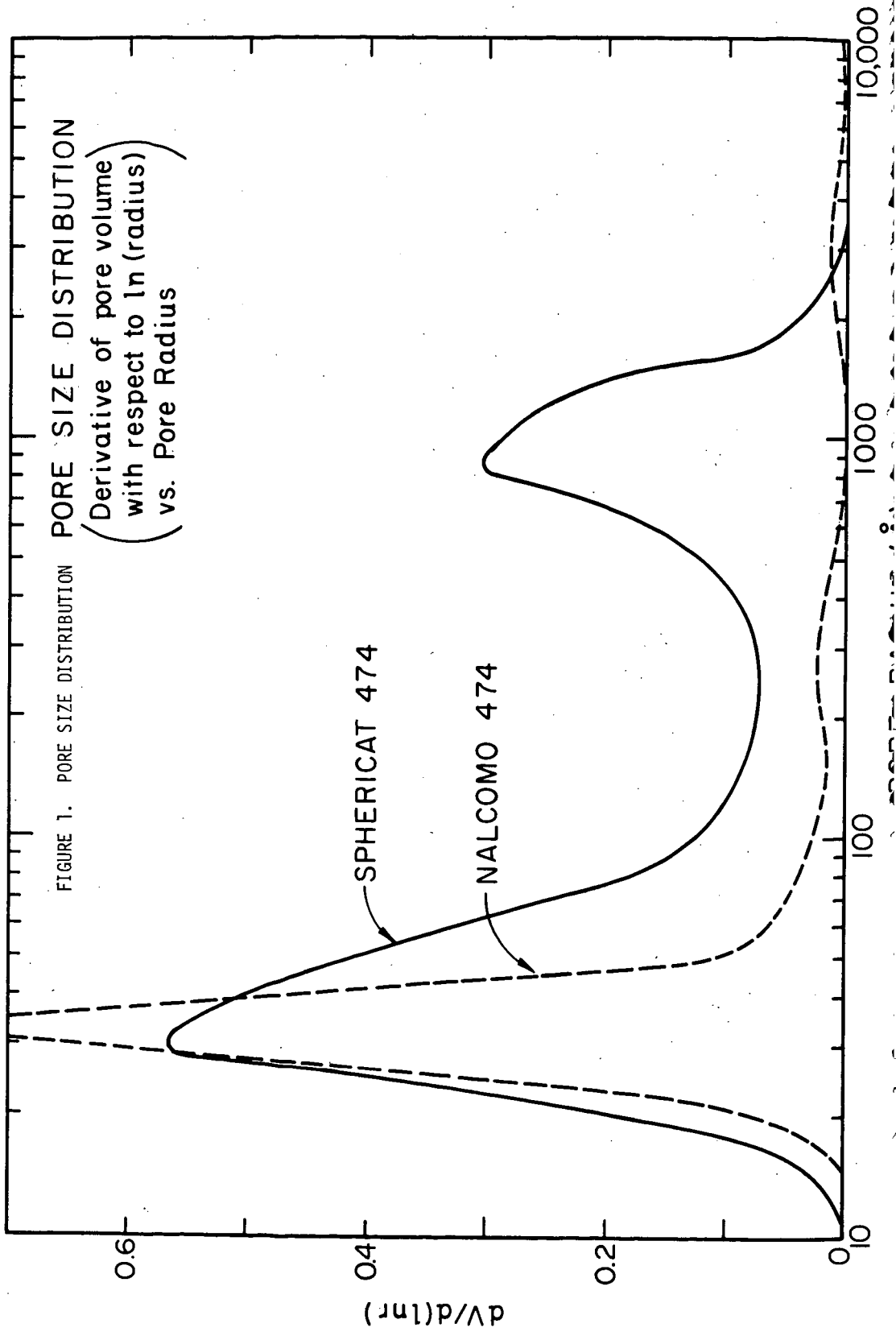
Average Formulas Suggested
For Coal Tar Components (9)

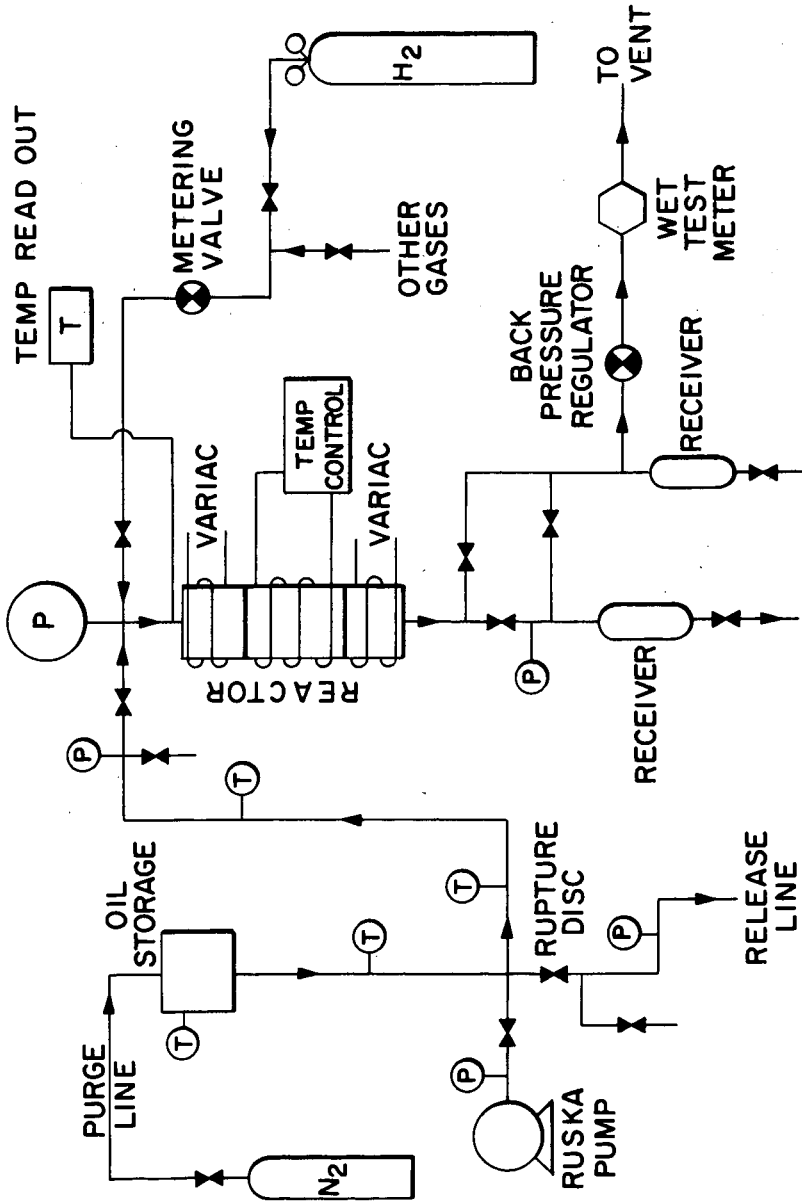
Phenanthridine

2, 4 - Dimethylbenzoquinoline

TABLE 5
CRITICAL DIAMETERS OF
SOME REPRESENTATIVE MOLECULES

<u>Molecule</u>	<u>Critical Diameter (A)</u>
Hydrogen	2.4
Hydrogen Sulfide	3.6
Methyl Mercaptan	4.5
Ethyl Mercaptan	5.1
Thiophene	5.3
Triethylamine	8.4





EXPERIMENTAL APPARATUS

FIGURE 2. EXPERIMENTAL APPARATUS

FIGURE 3 TYPICAL REACTOR TEMPERATURE PROFILE

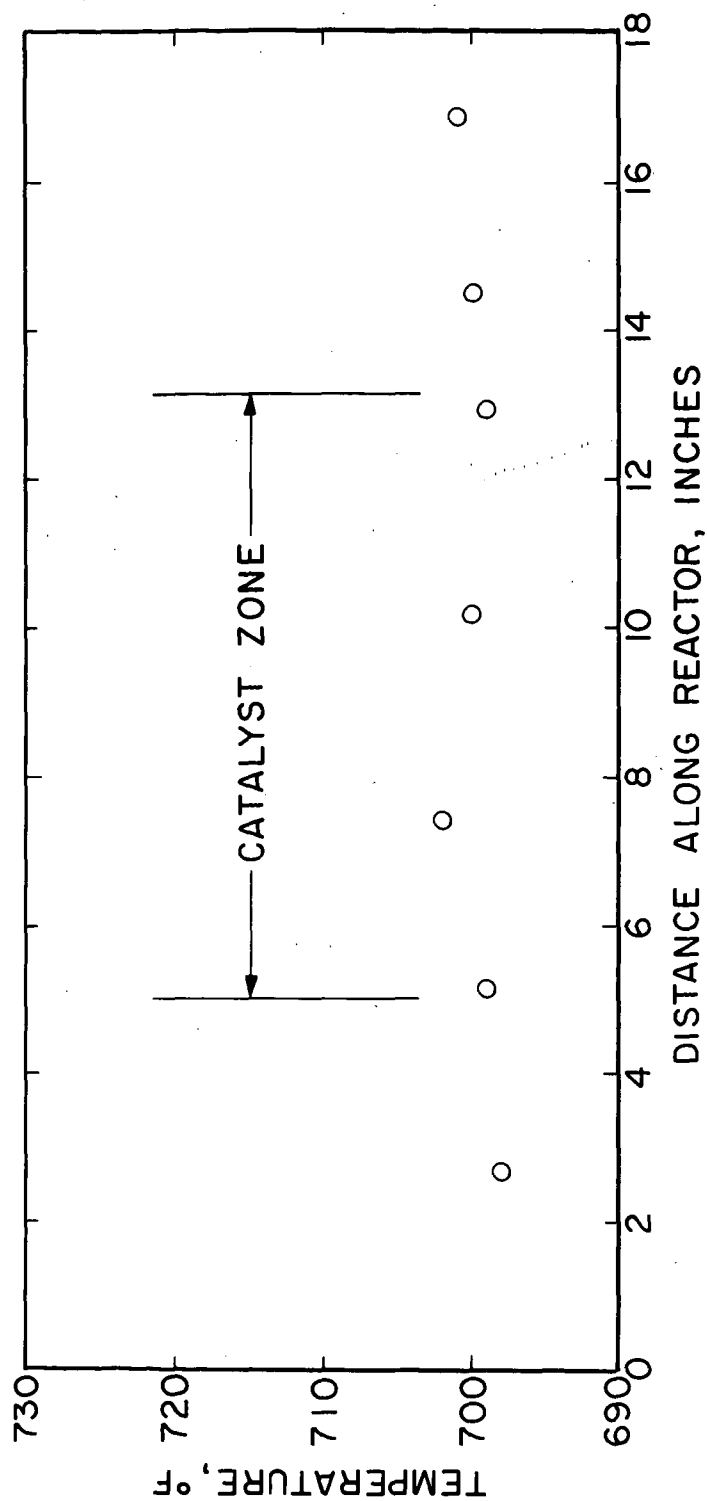


FIGURE 4
PERCENT SULFUR REMOVAL
AT VARIOUS SPACE TIMES-500 PSIG

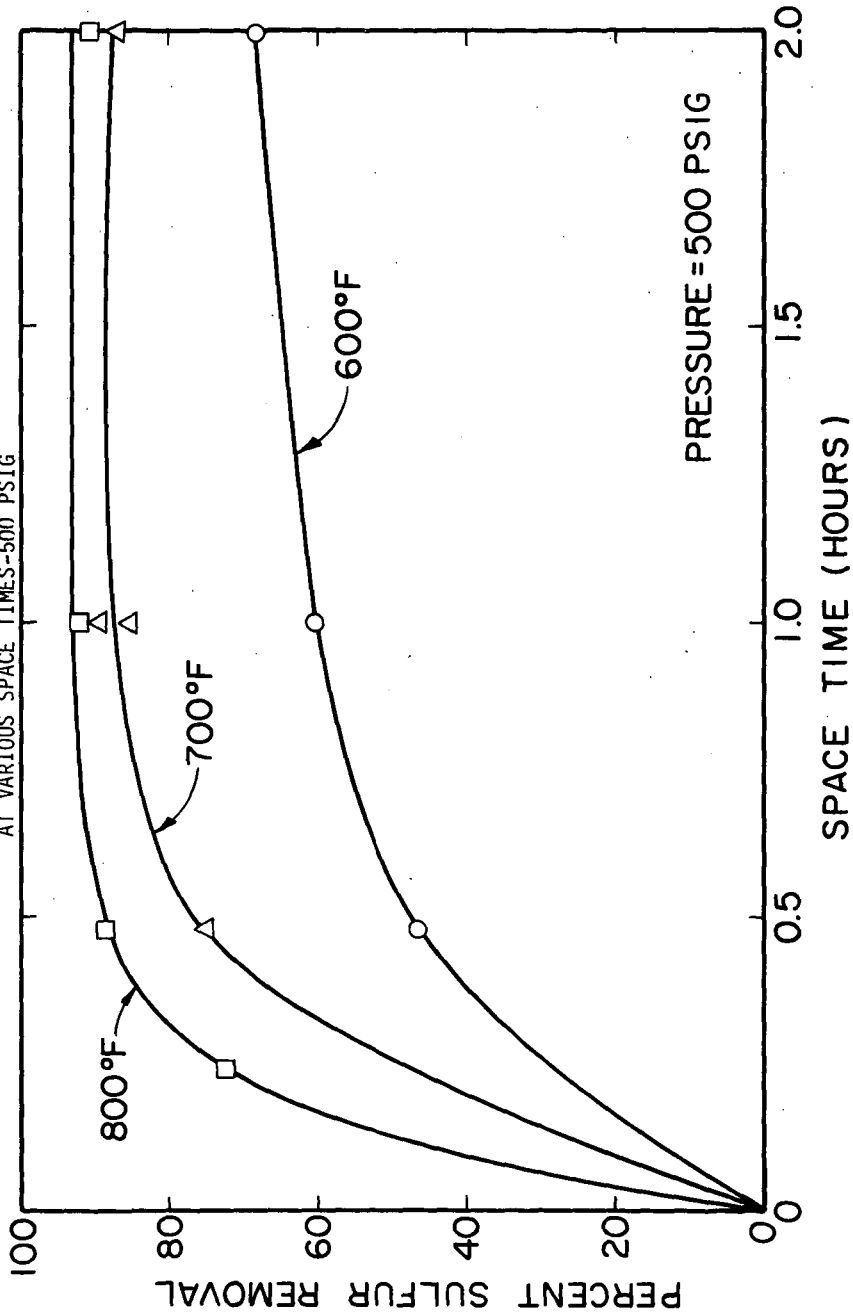


FIGURE 5
PERCENT SULFUR REMOVAL
AT VARIOUS SPACE TIMES-1000 PSIG

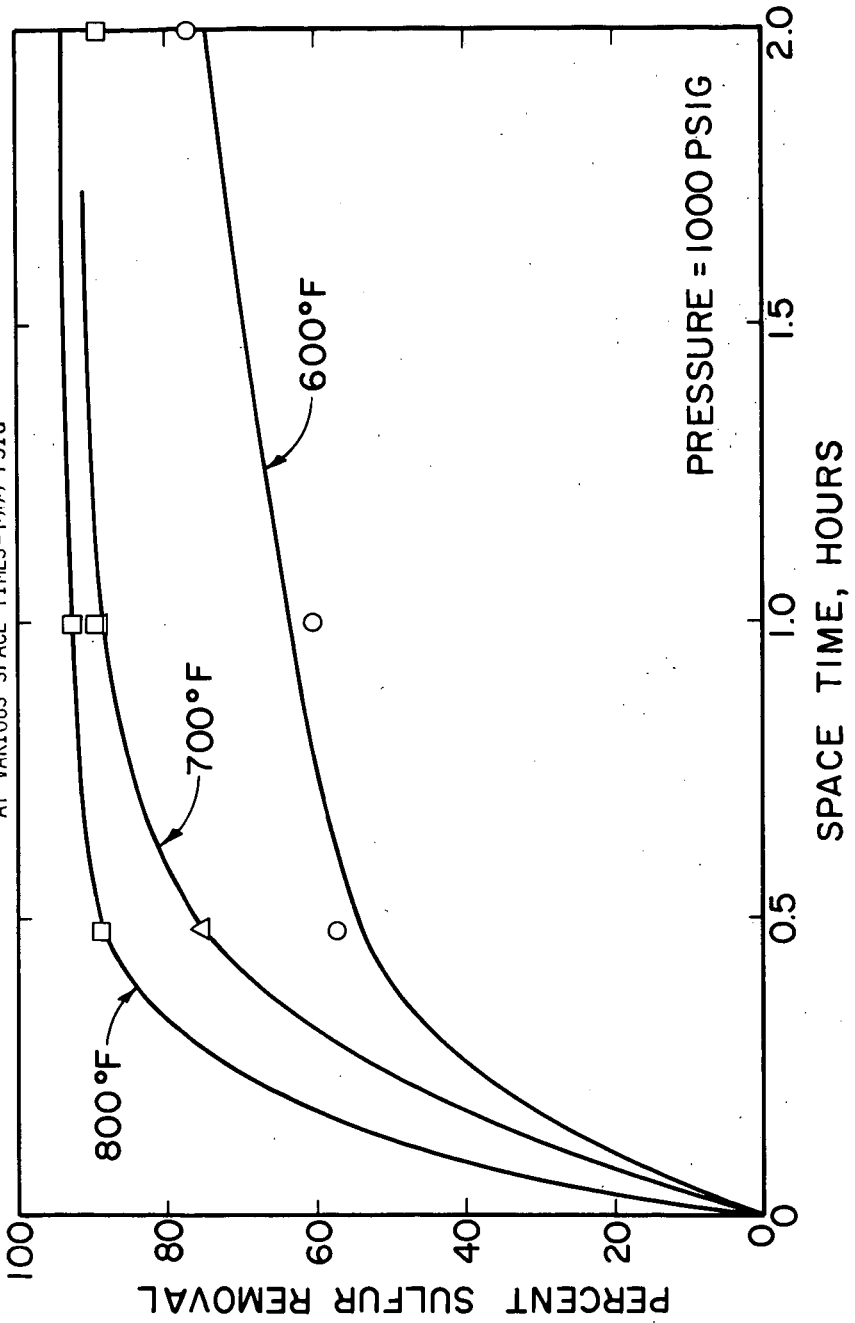


FIGURE 6
PERCENT SULFUR REMOVAL
AT VARIOUS SPACE TIMES-2000 PSIG

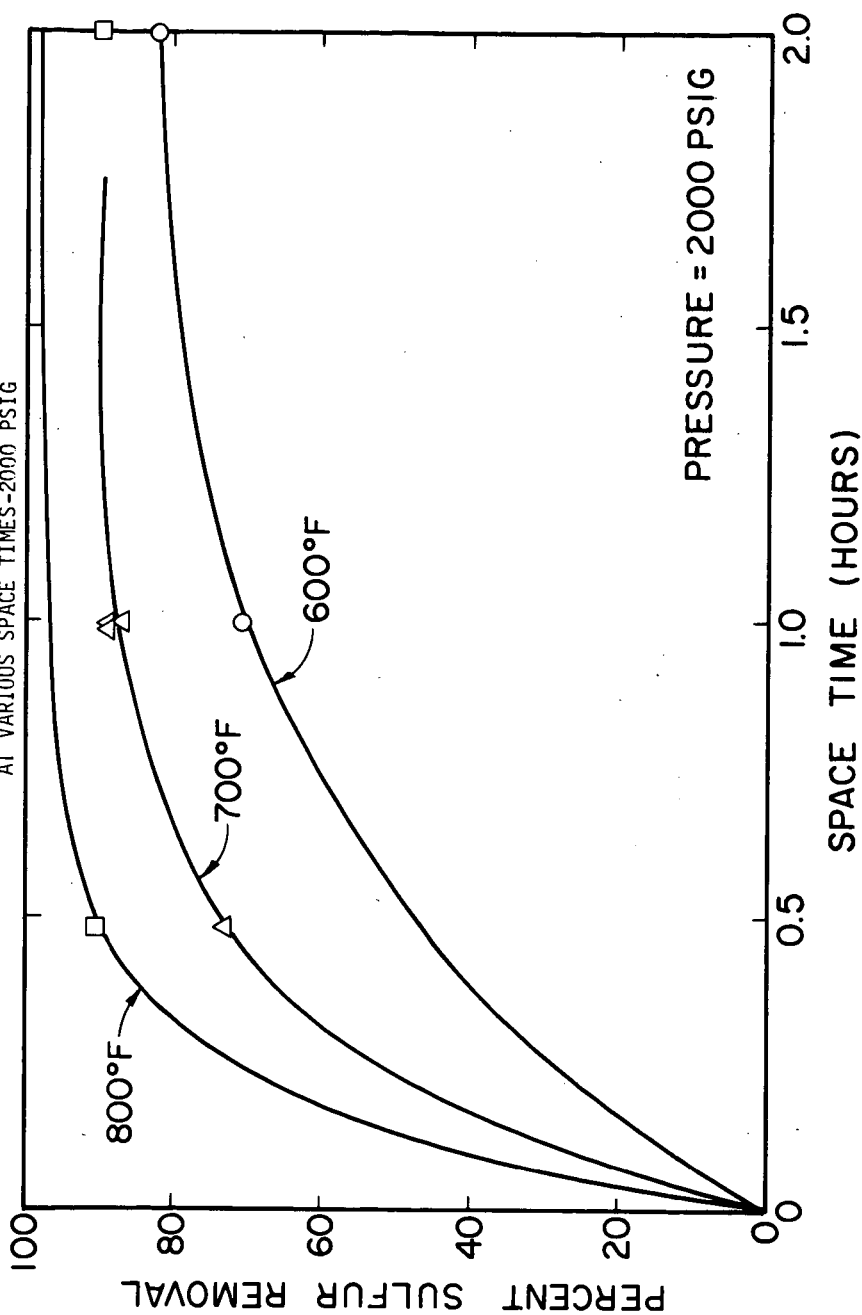


FIGURE 7
SULFUR REMOVAL AS FUNCTION
OF CATALYST AGE

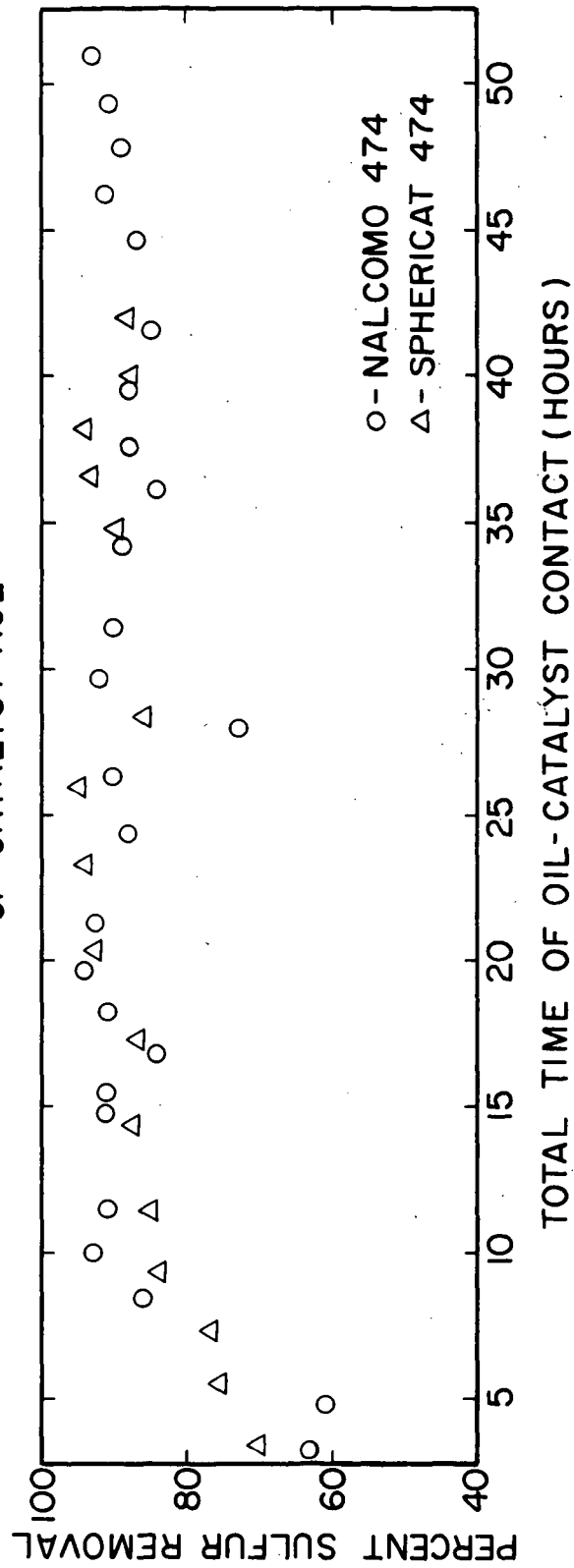
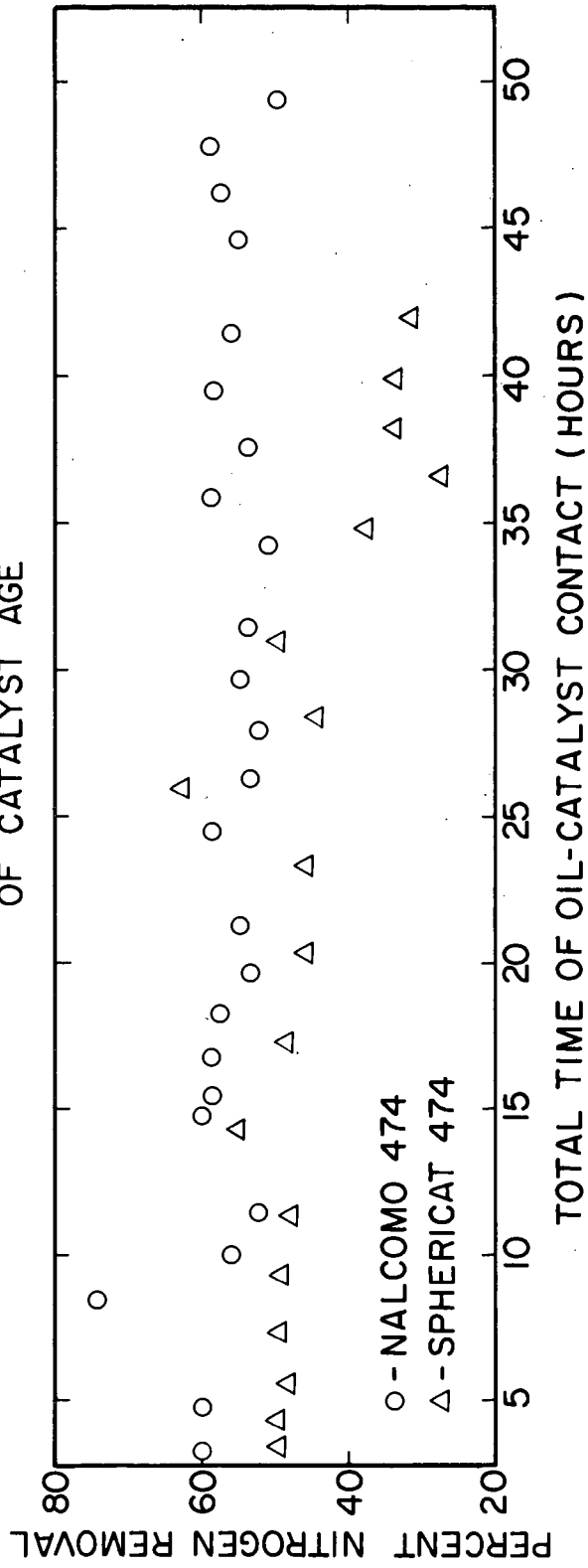


FIGURE 8
NITROGEN REMOVAL AS FUNCTION
OF CATALYST AGE



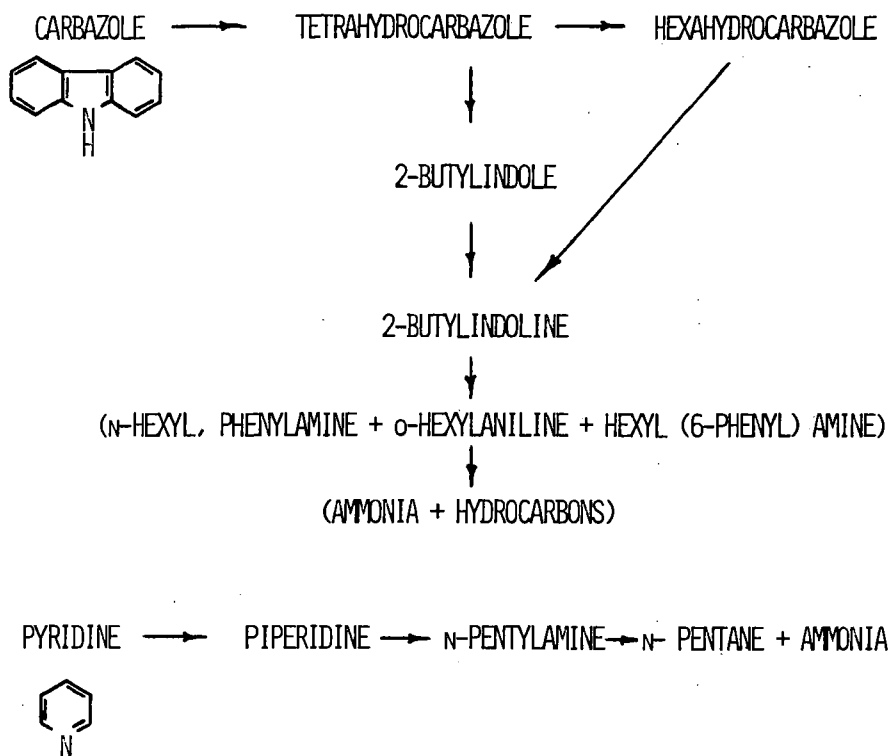
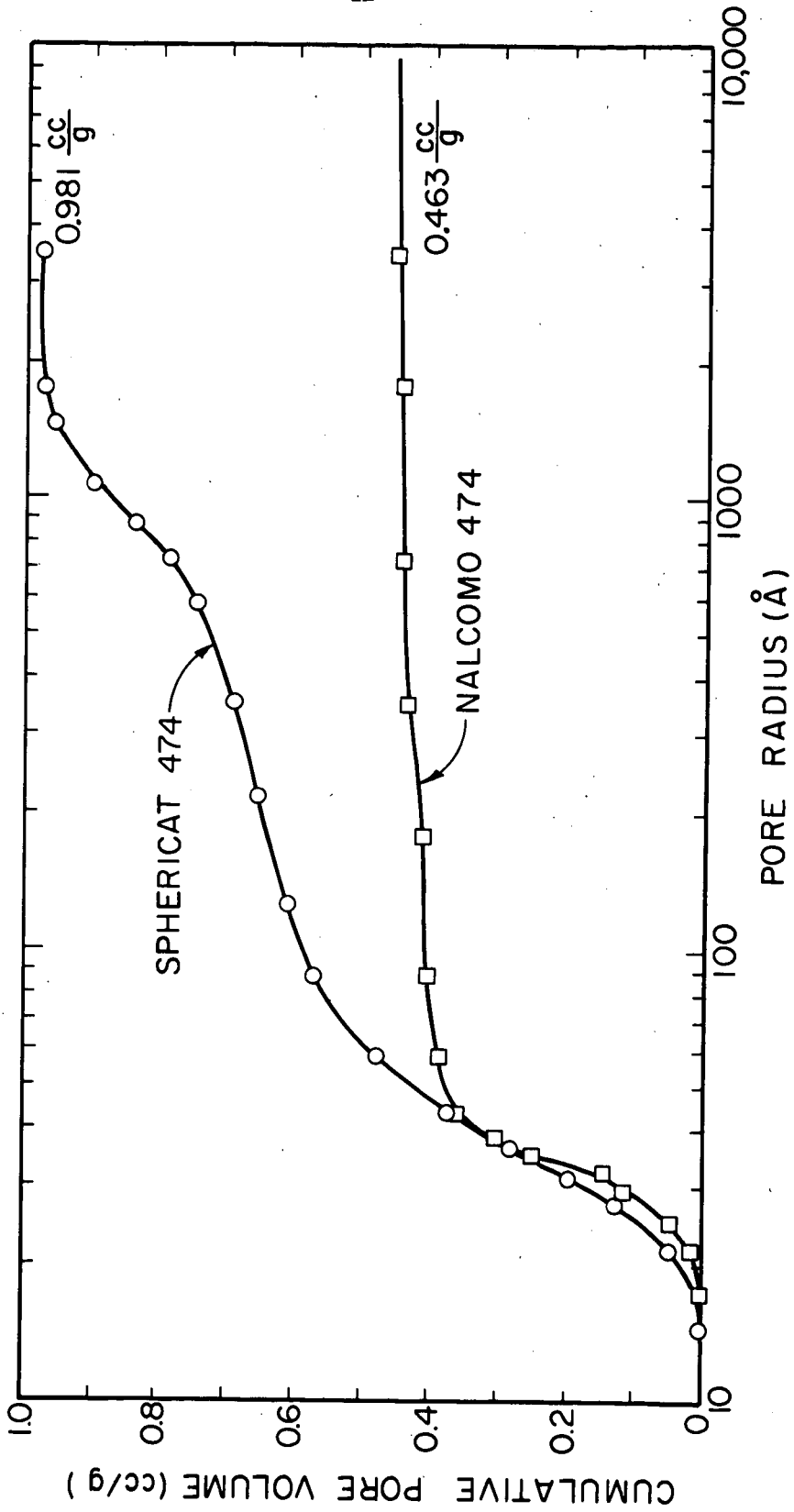


FIGURE 9

REACTION SEQUENCES FOR DENITROGENATION

FIGURE 10
CUMULATIVE PORE VOLUME
AS A FUNCTION OF PORE RADIUS



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